1.12 Chemical Processors shall demonstrate a familiarity level knowledge of techniques for environmental compliance-related sampling and monitoring.

Supporting Knowledge and/or Skills

a. Describe the types of equipment used to monitor a site for the following:

- Ambient air quality
- Emissions
- Groundwater
- Meteorological factors
- Streams and rivers
- Soil and sediment
- Wildlife

This section relies heavily on the document developed by EPA, A Compendium of Superfund Field Operations Methods, 1987, NTIS, Washington D.C.

- **Ambient Air Quality**

The **high volume particulate sampler** is used to sample organic compounds and associated particles in low vapor pressures in ambient air. Low vapor pressure components require filtration of large volumes of air to remove the particles. Substances examined include volatile, semivolatile, and nonvolatile organic compounds through the use of a high volume filtration device and sorbent filtration media. Limitations exist in the separation of highly polar organic compounds from the filter matrix for analysis.

All methods require a separation from sorbent to isolate compounds of interest. Solid sorbents are not compound-specific, resulting in the collection of unwanted compounds along with the target compound, requiring isolation of the target compound prior to analysis.[1] Organic polymeric sorbents collect minimal amounts of water (which can affect sample quality) but are unable to capture highly volatile organic compounds and certain polar compounds.[1] Inorganic sorbents (silica gel, alumina, and molecular sieves) have greater efficiency in collecting polar compounds, but capture water also, which accelerates their deactivation. Carbon sorbents are less reactive to water, are relatively nonpolar, and exhibit much stronger adsorption properties than organic sorbents, allowing efficient collection of VOCs such as vinyl chloride. Carbon sorbents also require the use of a solvent to displace the contaminant of concern from the sample matrix, with the potential of influencing the sample test results.[1]

Liquid bubblers are used to measure concentrations of SO_2 and O_3 in the atmosphere. Bubblers have been used to measure vertical gradient concentrations of these substances in studies of turbulent exchange of trace gases. Bubblers are constructed to provide long-term reliability, but as they employ a liquid collection medium, substantial changes can occur to the analyte. In addition, bubblers are not recommended for use in long-term monitoring in the United States because of rapid evaporation and chemical speciation.[1]

A nondispersive **infrared (IR) spectrometer** is most commonly used to measure carbon monoxide (CO). Infrared light attenuation is analyzed in comparison to a reference cell (containing a known quantity of CO). The limit on detection for airborne instruments is approximately 50 parts per billion (ppb) with a time resolution of 10 seconds.[1] Nitric acid can be detected by using Fourier transform infrared spectroscopy to a level of 4 ppb. An IR-tunable diode laser spectroscope will detect nitric acid at a level of 100 parts per trillion (ppt). Using IR-laser backscattering, sulfuric acid is detectable to less than 1g/m^3.

- **Emissions**

Emissions are sampled and analyzed using the same types of equipment and techniques (to detect the same type of substances) as listed under ambient air quality. Sampling and analysis procedures for pollutants from stationary sources are listed under 40 CFR Part 50.

The term “effluent” refers to something that flows out into the environment. At DOE sites, effluent air refers to air emissions released to the environment from processing and laboratory facilities. Ventilation and filtration systems constantly filter the air while monitoring equipment measures emissions to the environment.

Radionuclides, such as plutonium, uranium, and americium, occur as solid particles. As a result, particle filtration of airborne effluent streams is an important and effective means of preventing the release of these materials into the environment. Radioactive particles enter exhaust air streams where the particulate materials are removed by High Efficiency Particulate Air (HEPA) filters.

HEPA filters are designed to be fire- and chemical-resistant. They are constructed of tiny glass fibers combined with a small amount of organic material added for strength and water repellency. Multiple banks of HEPA filters, called filter plenums, are installed in series in air exhaust systems.

At regular intervals, particulate material samples from continuous sampling systems are removed from the exhaust systems and radiometrically analyzed for long-lived alpha emitters. Composite samples can be subjected to radiochemical separation and alpha spectral analysis, which quantifies specific alpha-emitting radionuclides. Bubble-type samplies are used to determine tritium concentrations and are measured using a liquid scinitllation photospectrometer.

- **Groundwater**

Monitoring groundwater contamination is accompished through collection of groundwater samples from a series of wells. A series of wells if typically installed to define the extent of contamination and to determine whether a “plume” of contamination exists. A number of wells are required to ascertain the direction of flow and rate of movement. Baseline conditions, which provide a basis for comparison, can be determined by collecting samples from nearby wells that are known to be free of contaminants.

Table 1.33.1 lists some of the devices used for sampling groundwater quality monitoring wells:

Table 1.12-1
Groundwater Sampling Devices[2]

Type	Advantages	Disadvantages
Bailer	Can be constructed in a wide variety of diameters.	Sampling procedure is time consuming; sometimes impractical to properly evacuate casing before taking samples.
	Can be constructed from a wide variety of materials.	Aeration may result when transferring water to the sample bottle.
	No external power source.	
	Extremely portable.	
	Low surface-area-to-volume ratio, resulting in a very small amount of outgassing of volatile organics while sample is contained in bailer.	
	Easy to clean.	
	Readily available.	
	Inexpensive.	
Suction-lift Pump	Relatively portable.	Sampling is limited to situations where water levels are within about 20 ft of the ground surface.
	Readily available.	Vacuum effect can cause the water to lose some dissolved gas
	Inexpensive.	
Air-lift Samplers	Relatively portable.	Causes changes in carbon dioxide concentrations; therefore, this method is unsuitable for sampling for pH-sensitive parameters.
	Readily available.	In general, this method is not an appropriate method for acquisition of waste samples for detailed chemical analyses because of degassing effect on sample.
	Inexpensive.	
	Suitable for well development.	
Gas-operated Pump	Can be constructed in diameters as small as 1 inch.	Gas source required.
	Can be constructed from a wide variety of materials.	Large gas volumes and long cycles are necessary when pumping from deep wells.
	Relatively portable.	Pumping rates are lower than those of suction or jet pumps.
	Reasonable range of pumping rates.	Commercial units are relatively

		expensive.
	Driving gas does not contact water sample, eliminating possible contamination or gas stripping.	
Submersible Pump	Wide range of diameters.	With one exception, submersible pumps are too large for 2-in diameter pumps.
	Constructed from various materials.	Conventional units are unable to pump sediment-laden water without incurring damage to the pump.
	12-volt pump is highly portable; other units are fairly portable.	1 3/4-inch pump delivers low pumping rates at high heads.
	Depending on size of pump and pumping depths, relatively large pumping rates are possible for wells larger that 2-in diameter.	Smallest diameter pump is relatively expensive.
	1 3/4-inch helical screw pump has rotor and stator construction that permits pumping fine-grained materials without damage to the pump.	

Pressure-vacuum **lysimeters** are predominately used in the unsaturated zone to obtain samples of in situ soil water. They consist of a porous ceramic cup capable of holding a vacuum, a small-diameter sample chamber made of PVC pipe and two sampling tubes leading to the surface.

A **piezometer** measure the hydraulic head of groundwater and is frequently used for monitoring water pressure in earthen dams, under foundations, or in aquifers. It can also be used to measure vertical head differences under unconfined conditions. Piezometers are also used to monitor water levels similar to a monitoring well.

A **tensiometer** consists of a porous cup attached to an airtight, water-filled tube. The porous cup is inserted into the soil at the desired depth, where it comes into contact with the soil. After hydraulic equilibrium with the soild is reached, water moves through the porous cup from the tube into the soil. A vacuum is created at the top of the airtight tube and is a measure of the negative pressure head in the soil. The measured pressure head is used to determine the hydraulic head.

- **Meteorological Factors**

Site-specific meteorological data are preferred when conducting screening or refined model analyses. Collection of meteorological data in the field requires the design of a system that provides the necessary input information for dispersion modeling and takes into account the logistics of siting and operation. The following are meteorological parameters that are usually defined in the field:

Horizontal wind speed sensors (anemometers) are available in many shapes and sizes. The most common types are the rotational cup and the propeller anemometers. The cup sensors are generally more accurate. The design of the anemometer cups dictates the durability, sensitivity, accuracy, and response of the instrument. Three conical cups usually provide the best performance. Propeller anemometers revolve around a pivoted shaft, which is oriented by a vane, into the direction from which the wind is blowing. The number of blades normally varies from three to six. For most atmospheric dispersion studies, anemometers should have a starting threshold of 0.5 meters per second or less and a system accuracy of ± 0.2 meters/sec.

Most sensors for measuring **horizontal wind direction** consist of a vane rotating on a fulcrum. The shapes and designs of the vane surface vary but are generally rectangular or curved. The vanes are designed to orient into the direction from which the wind is blowing. For atmospheric dispersion studies, wind vanes should have a starting threshold of less than or equal to 0.5 m/s and a system accuracy of ± 5 degrees.

Vertical wind speed and direction can be measured with a vertical propeller anemometer, a UVW anemometer, or bivane. The vertical propeller anemometer has a propeller-type sensor mounted on a fixed vertical shaft. Since the propeller can reverse its direction, the sensor can indicate whether wind flows are directed upward or downward. The UVW anemometer is located on a vertical shaft at right angles to the first two shafts. This anemometer will measure the total (i.e., U and V and W are the horizontal winde components, and W is the vertical wind component) wind vector. The UVW anemometer can be assembled to give real time data, including wind speed, azimuth, and elevation. The bivane consist of a vane with two flat plates perpendicular to each other and mounted so as to allow rotation horizontally and vertically. It only provides azimuth and elevation components of the wind direction and, therefore, must be complemented with a propeller anemometer.

The most common devices used are resistive temperature detectors (RTDs) and thermistors. Thermistors are electronic semiconductors that are made from certain metallic oxides. The resistance of the thermistor varies inversely with its absolute temperature so the electrical output through the sensor can provide an indication of the **ambient temperature**. The RTD is used in a similar manner. These RTD sensors are made of different pure metals such as silver, copper, nickel, or platinum. Normally, platinum provides the best material. The RTD operates on the principle that the electrical resistance of a pure metal increases with temperature.

Cloud cover is best determined from data collected at a representative National Weather Service (NWS) station where trained observers are available to provide this information. If representative NWS cloud cover data are not available, the total amount of cloudiness above the apparent horizon should be estimated as a fraction (in tenths) by a visual observation.

Ceiling height is defined as a layer of clouds that cover more than one-half of the sky. The height of a ceiling is best determined by experienced observers at NWS stations. It can be estimated visually at the waste site by determining the height of the lowest layer of clouds that cover more that 50 percent of the sky. A pocket-sized cloud atlas may be a useful tool for the field observer.

Mixing heights are best determined from representative NWS stations that record upper air (i.e., above the surface) data. Instrumentation packages called radiosondes are carried aloft twice daily (7:00 a.m. and 7:00 p.m. EST) throughout the United States by nontethered balloons. These packages measure wind speed and direction, temperature, and humidity as they ascend. Estimates of the mixing height can also be made at the site through the use of balloonsondes (tethered and nontethered balloons) and with remote sensors, such as acoustic sounders. This equipment requires special expertise to use, evaluate, and apply the collected data.

Atmospheric stability is determined in the field by using a number of alternative methods. The Pasquill-Turner method uses onsite data, which includes cloud cover, ceiling height, surface winds (approximately 10m height), the Sigma phi method, the Sigma theta method, and the Pasquill-Turner method using onsite wind speed with cloud cover and ceiling height from a nearby NWS site[3]

- **Streams and Rivers**

Samples from shallow depths can be readily collected by submerging the sample container. The sample container is usually disposable or constructed of a nonreactive material, such as glass, stainless steel, or Teflon. For this type of sampling, a weighted-bottle sampler is used to collect samples at any predetermined depth. The sampler consists of a glass bottle, a weighted sinker, a bottle stopper, and a line used to open the bottle and to lower and raise the sampler during sampling.

Teflon bailers have also been used where feasible for collecting samples in deep bodies of water. Where cross-sectional sampling is not appropriate, near-shore sampling may be done using a pond sampler.

Another method of sampling requires the use of a peristaltic pump. The pump can be attached to a long arm, allowing for the sample to be pumped directly to the sample container. This system allows the operator to reach into the liquid body, sampling from depth, or sweeping the width of narrow streams.

- **Soil and sediment**

Sediments near shore or above the waterline are most easily collected using simple tools, such as polypropylene scoops, trowels, or dippers. Other alternatives for small semi-solid sediments include wooden tongue depressors or stainless steel tablespoons. For stream bottom samples of sediment, vertical pipe or core samplers (hand corers, gravity corers) are used and can be driven into stream beds to any selected depth. Ponar grab samplers are a clamshell-type scoop activated by a counter lever system. The shell is opened, latched in place, and slowly lowered to the bottom. When tension is released on the lowering cable, the latch releases and the lifting action of the cable on the level system closes the clamshell.

- **Wildlife**

General collection of terrestrial vertebrates will document the presence of species. Collection techniques can be used to estimate population sizes. Vertebrate collection can be used to gather tissue for pollutant analysis.

Live trapping can be used for collection of sensitive species when lethal traps or hunting would be inappropriate. Population sizes can be estimated using live traps in a mark-and-recapture context. A list of species present on the site can be generated. The size of the range can be estimated using marking or radiotelemetry after capture and release. In addition, animals can be trapped live to collect tissue (especially blood) for analysis.

Lethal trapping can be used to establish which species are present on a site and to collect tissue-donor specimens for analysis of pollutants.

Hunting allows the documentation of species present on the site and is suitable for collecting tissues for analysis. It is most useful on medium- to large-sized species and may be best for species not susceptible to trapping.

Ecological analysis, or Habitat Evaluation Procedure (HEP), provides an integrated analysis of the habitat values on a site. The impact of pollution on the site's most important habitat values can be assessed by using an uncontaminated comparison area or information on a polluted site before it was polluted.

Macroinvertebrates can be sampled using sediment grabs, core samplers, shovels, box sieves, surber samplers, invertebrate drift nets, traps (i.e., lake bottoms for crayfish), artificial substrates, in situ bioassays and other miscellaneous methods (i.e, hands, hand tools, dip nets, plankton nets).

Methods for collecting **fish** samples include trawls, electrofishing, seining (large net fishing), hook and line, and miscellaneous (i.e., gill nets, trammel nets, fyke nets, or rotenone) methods.

b. Explain the reason for measuring emissions, meteorological factors and ambient air quality under the various operating conditions (e.g., routine or emergency).

Measurement of emissions from stationary sources is required under the Clean Air Act and State Implementation Plans to comply with permit conditions (40 CFR Part 50 Subpart F). Monitoring demonstrates operational compliance or violation of permit conditions and the need for corrective action. To properly evaluate measured emissions (and establish a pre-permit conditions baseline), factors influencing the established operational limits, such as ambient air conditions and meteorological factors, must be considered. Wind direction, temperature, air pressure, relative humidity, and other meteorological conditions will affect the data collected on ambient air quality and emissions. Meteorological factors are critical to establishing dispersion patterns of pollutants and relative risk posed to populations in emergency conditions.

c. ***Describe the purpose for measuring each of the following parameters during field surveys of water quality:***

- Temperature
- Dissolved oxygen
- Conductivity
- pH

The Federal Water Pollution Control Act (FWPCA) of 1972 was passed to restore and maintain the chemical, physical, and biological integrity of the Nation's waters, to be achieved by characterization of stream conditions and wastewater effluents. Under the FWPCA, the primary characteristics of interest were biological oxygen demand (BOD), chemical oxygen demand (COD), solids, conductivity, pH, oil and grease, fecal coliform, heavy metals, and select organic compounds. These substances under consideration effectively defined the criteria for water quality and the substances to be investigated in determining compliance[1].

To adequately determine conditions in existence prior to permitting of a facility to discharge effluents, a baseline of the conditions in the receiving body of water must be established. This baseline is instrumental in determining what effluents can be discharged in what quantity without affecting water quality and use. During operation and discharge, stream water quality must be monitored to assure that the facility is discharging in compliance with its permit.

Temperature, dissolved oxygen, conductivity, and pH are general indicators of the health of a water body, including the ability to sustain aquatic life. These parameters also give an indication of the redox potential of the water body.

Additionally, measurement of these criteria can be indicative of sample quality. **Temperature** is taken in the field because conductivity and pH are temperature dependent and may be altered in transport from the well head to the laboratory. Also, prior to collection of a ground water sample, the temperature should equilibrate over at least three casing volumes, indicating that the groundwater sample is indeed from the aquifer and not from water influenced by the installation of the monitoring well[1]. Temperature also affects solubility of pollutants and may be indicative of the release of contaminants in general (i.e., increase in temperature due to pollutant chemical reactions).

Dissolved oxygen (DO) is measured because groundwater is usually nearly oxygen free (possessing dissolved ions in their most reduced state), the presence of dissolved oxygen in a groundwater sample calls into question the sample collection method[1]. DO also affects the rates of chemical reactions and indicates the presence of pollutants.

Conductivity of a groundwater sample is dependent upon the total dissolved solids (TDS) content of the sample. Because TDS concentration and conductivity of a sample may be pH dependent, measurement of the conductivity should occur in the field along with the measurement of pH. The value for conductivity should be stable over three well casing volumes to ensure proper sample representation of the aquifer. Conductivity also measures salinity and indicates the ability of a water body to carry electrical current.

The **pH** measures the acidity and alkalinity of a water body and is indicative of contamination. The pH of a sample is taken in the field at the moment of sampling to document the original conditions of the aquifer. Once water is put into a sample bottle, the measured pH at the laboratory may not have any relation to the original conditions of the aquifer. Additionally, many analytical parameters are pH dependent and therefore may change concentration based on the value of pH. Thus, field measurement of pH is standard practice for groundwater sampling.

d. Discuss the factors that can affect readings and the preservation methods for the field measurements listed above.

At the moment of sample collection, chemical and physical processes that affect the sample may be altered, in some cases rendering the sample as nonrepresentative of existing water quality. Exposure of well samples to light and temperature variations can cause photochemical reactions and temperature-dependent kinetic reactions, altering the sample. Additionally, exposure to atmospheric conditions at ground level will change the composition of dissolved gases within the sample. The pH of the sample may also change due to these reactions.

Samples are vulnerable to changes resulting from reaction of constituents with materials in the sample container, resulting in the loss of volatiles or the addition of extraneous compounds.[1] **Volatilization** should be minimized by containing the sample in a vessel with no head space. **Adsorption and absorption** can be minimized by using a container lined with the proper material for the substance being considered (i.e., plastic containers for solutions containing metals, glass containers for solutions containing oils, etc.). **Diffusion** is minimized by containerizing the sample in Teflon-lined vessels. **Precipitation** is caused by a change in pH of the sample solution due to a reaction with the atmosphere, and can be offset by the addition of nitric acid to the solution until its pH is less than 2. **Chemical changes** require the use of specific control procedures for specific compounds and are beyond the scope of this study guide. Refer to the analytical method associated with the analyte of concern for recommended preservation techniques. The minimization of **photochemical changes** requires collection of samples in amber glass or the proper opaque container. **Microbiological degradation** is offset by controlling pH and temperature of the sample. Extreme pH (low or high) and low temperatures can be effective, as can the addition of certain preservatives which kill and fix the organisms in the sample.[1]

e. Describe how trace toxic organics, volatile organics, and heavy metals are measured.

Trace toxic organics - An example of an assay of trace toxic organics using gas chromatography (GC) is found in the EPA methods for analysis of pesticides in drinking water. The EPA method for detection of pesticides in drinking water require the use of GC with the proper detector (ECD or NPD); or the use of GC in conjunction with mass spectroscopy (MS); or through the use of compound-specific methods (EPA methods 507, 508, 515.1, 53.11, and 504).[1] Techniques common to these methods include sample collection, preservation, and storage at 4°C; descriptions of required apparatus and equipment; safe handling procedures pertaining to reagents, consumables, and standards; the use of two columns of different polarity; and instructions on the use of blank samples, internal standards, surrogate solutions, interferences, calibrations, standardization, and quality control.[1]

For example, EPA Method 505 for the analysis of organohalide pesticides and PCB products in water (by microextraction of GC-ECD) requires following the following procedure:

- **Method summary -** 35 ml of sample is extracted with 2 ml of dichloromethane, 2 μl is injected onto the GC-ECD (extraction and analysis time = 30-50 minutes);
- **GC columns used -** primary column = 0.32mm i.d. x 30m long, fused silica capillary column with DB-1; confirmatory columns = 0.32mm i.d. x 30m long, fused silica capillary columns with 1:1 mixed phase dimethylsilicone and polyethylene glycol (Durwax - DX3) or equivalent, or 0.32mm i.d. x 25m long 50:50 methyl-phenylsilicone (OV-17) or equivalent; and,
- **Method detection limits -** (MDLs) only for modern pesticides (μg/l) at: Arochlor = 0.075, Atrazine = 2.4, Metoxychlor = 0.96, and Simazine = 6.8.[1]

Volatile organics - In air sampling for volatile organic compounds (VOCs), large volumes of air (2-100L) are forced through a solid sorbent material for adsorption of the compound to be examined. Separation of unwanted compounds from the target compound is made, followed by analysis of the sample through the use of gas chromatography.

Heavy metals - Atomic absorption (AA) spectroscopy is the most widely used method of measurement of metals in water because it is highly sensitive and specific (only one metal can be tested at a time). AA has the ability to measure for certain trace minerals in fresh water without sample preconcentration. Atoms absorb light in the ultraviolet-visible spectrum by interaction with a photon and an electron transition from a ground state to an excited state.

This procedure requires the conversion of the metal in the sample into a gaseous state in the sample matrix, as free atoms are necessary for atomic absorption to take place. The conversion of the sample metal into a gas is achieved through aspiration of the metal solution into a flame, through use of a graphite furnace, or by chemical reduction in a solution followed by air bubbling. A gas stream combines with the vapor, forcing it into an Ar-H_2 airflame, where concentration of the substance is measured. As atomic spectra have distinct profiles on the range of 0.2nm-wide, a monochometer is introduced into the system to disperse unwanted lines. The resulting profiles are analyzed.

[1] Keith, Lawrence H. (editor), *Principles of Environmental Sampling*. Salem, MA, American Chemical Society, 1988.
[2] Driscoll, F., 1986. *Groundwater and Wells*. 2 ed. Johnson Division, St. Paul, Minnesota. P. 729.
[3] U.S. EPA, Evaluation Guidelines for Toxic Air Emissions from Land Disposal Facilities. Washington D.C., Office of Solid Waste. August 1981